Evidence for a Nodal-Line Superconducting State in LaFePO

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In several iron-arsenide superconductors there is strong evidence for a fully gapped superconducting state consistent with either a conventional s-wave symmetry or an unusual $s_{\pm}$ state where the gap changes sign between the electron and hole Fermi-surface sheets. Here we report measurements of the penetration depth $\lambda(T)$ in very clean samples of the related iron-phosphide superconductor, LaFePO, at temperatures down to $\sim$100 mK. We find that $\lambda(T)$ varies approximately linearly with T strongly suggesting the presence of gap nodes in this compound. Taken together with other data, this suggests the gap function is not universal for all pnictide superconductors.

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A key question in understanding the physics of the recently discovered iron pnictide superconductors is what is the origin of the pairing interaction. Measurements of the symmetry and anisotropy of the superconducting energy gap are very useful for helping to decide between competing theories. Although several experiments designed to deduce the gap anisotropy have been performed, a consensus has not yet been reached.

Several experiments indicate that the gap is finite at all points on the Fermi surface, however, others have suggested the presence of pronounced gap anisotropy or nodes. The presence of a fully gapped state is supported by point-contact tunneling spectroscopy measurements of $SmFeAsO_xF_y$ (Sm-1111) [1–3], penetration depth measurements of Pr-1111 [4], Sm-1111 [5], Nd-1111 [6], and $Ba_xK_yFe_2As_2$ (Ba-122) [7] and angle resolved photoemission measurements of Ba-122 [8–11]. Several of these measurements show evidence of two distinct gaps. On the other hand, some experiments suggest the presence of low energy excitations which could be indicative of nodes. These include nuclear magnetic resonance measurements of La-1111 [12,13] and penetration depth measurements of Co-doped Ba-122 [14,15].

Theoretically, there is considerable debate about the nature of the gap anisotropy and symmetry. Band-structure calculations have shown that both the 1111 and 122 materials have multiple quasi-two-dimensional sheets of Fermi surface, holelike close to the zone center and electronlike at the zone corner. At least for the undoped parent compounds these sheets are close to a nesting instability which can drive the system towards antiferromagnetism [16]. Several papers have argued that spin-fluctuations mediate the electron pairing and Mazin *et al.* [16] argued that this favors an $s_{\pm}$ paring state where both the electron and hole Fermi surfaces are *fully gapped* but with gap functions which are π out of phase. Others, however, have come to different conclusions. Most recently, Graser *et al.* [17] have calculated that the strongest pairing energy gap functions both have *nodes* on one or more of the Fermi surface sheets. One of these gap functions has s symmetry, but is distinct from the original $s_{\pm}$ state, whereas the other has d symmetry.

The iron-phosphide superconductor LaFePO is isostructural with LaFeAsO (La-1111). Its relatively low $T_c \sim 6$ K [18] has been linked to the fact that the Fe-P bond angles depart substantially from those of a regular tetrahedron [19]. Unlike the corresponding As-based compound, nominally undoped LaFePO is nonmagnetic and superconducting [20]. The electronic structure of LaFePO has recently been explored in some detail by de Haas–van Alphen (dHvA) measurements [21], which confirm the band-structure predictions of almost nested electron and hole pockets, a feature expected to be common to all Fe-pnictides not subject to antiferromagnetic Fermi-surface reconstruction. The detailed knowledge of the electronic structure and availability of superconducting samples with very low levels of disorder makes LaFePO an ideal material in which to study order parameter symmetry. In this Letter, we report measurements of the London penetration depth of LaFePO down to very low temperature $T < 0.02T_c$. Our data show strong evidence for the presence of line nodes in this compound.

Our samples were grown via a Sn flux method which produces platelike single crystals with typical dimensions 0.15 mm in the basal plane and $<$0.03 mm in the interlayer direction [20,22]. X-ray diffraction confirmed that the samples were of high crystalline quality [22]. The samples measured in this study are from the same batch as those used for dHvA measurements where the mean free path was estimated to be $\gtrsim$ 1000 Å for the electron sheets and $\sim$500 Å for the hole sheets [21]. Heat capacity, measured using a modulated temperature technique, on the same single crystals used for the penetration depth measurements confirmed the bulk nature of the superconductivity.

The data for sample 1 in Fig. 1 shows a sharp jump in C at T_c with the midpoint at $T \simeq 5.6$ K with width ~ 0.25 K. Radio frequency (rf) susceptibility measurements for the same sample (Fig. 1) show a diamagnetic superconducting transition with the same midpoint and width. Other samples measured in our study had T_c values in the range 5.4–5.9 K.

Measurements of the temperature dependence of the London penetration depth were performed with a high resolution susceptometer based on a self-resonant tunnel diode circuit which was mounted in a dilution refrigerator. The circuit operates at ~ 14 MHz with an extremely small probe field ($H_{ac} < 10$ mOe) so that the sample is always in the Meissner state [23]. Changes in the resonant frequency are directly proportional to changes in the magnetic penetration depth as the temperature of the sample is varied. The calibration factor is determined from the geometry of the sample, and the total perturbation to the resonant frequency due to the sample, found by withdrawing the sample from the coil at low temperature [24]. The sample is mounted on a sapphire rod, the other end of which is glued to a copper block on which the RuO_2 thermometer is mounted. The sample and rod are placed inside a solenoid which forms part of the resonant tank circuit. The position of the sample within the solenoid could be varied *in situ* allowing us to vary the rf probe field and hence check for rf heating which in principle could cause the thermometer and sample to be out of equilibrium. The sapphire sample holder has a very small paramagnetic background signal which varies $\sim 1/(T + \theta)$ but was too small to measure precisely and has not been subtracted. It corresponds to at most 20 Å between 100 and 200 mK.

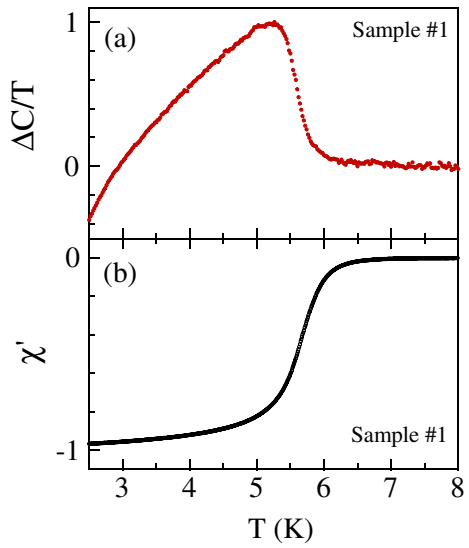

FIG. 1 (color online). (a) Heat capacity anomaly in a LaFePO single crystal. ΔC is the difference between the heat capacity data in zero field and for $B = 0.47$ T (where $T_c < 2$ K). (b) rf susceptibility of the same sample close to T_c.

Figure 2 shows the temperature dependence of the in-plane penetration depth, $\Delta\lambda_a(T)$ in three samples, all measured with the rf field directed perpendicular to the conducting planes so only in-plane screening currents are induced. The temperature dependence is very similar in all three samples and is approximately linear. A variable power-law fit, i.e. $\Delta\lambda(T) \propto T^n$ for $T < 1$ K gives $n = 1.2 \pm 0.1$. The close to linear temperature dependence of λ is strongly indicative of nodes in the order parameter.

The temperature dependence of λ arises from the depletion of the screening superfluid by thermal excitations. The superconducting energy gap Δ_k dictates the spectrum of these excitations; if Δ_k is finite for all momentum wave vectors, an exponential temperature dependence of $\lambda(T)$ is observed. By contrast, in a superconductor with an unconventional pairing symmetry the order parameter passes through zero for some wave vectors, leading to the presence of low energy excitations down to low temperatures and a power-law temperature dependence of the penetration depth. In a clean superconductor with line nodes on a quasi-2D Fermi surface the angular averaged density of states has a linear energy dependence, leading to a linear behavior of $\lambda(T)$ at low temperature.

The approximately linear temperature dependence in LaFePO is in marked contrast with that observed in conventional superconductors, or those displaying anisotropic s-wave superconductivity, such as MgB_2 or $NbSe_2$ [25,26], or the As-based 1111 compounds described in the introduction. In an s-wave multiband superconductor the low

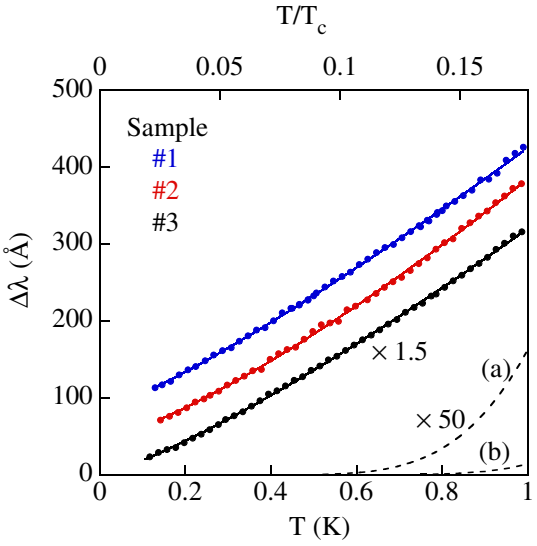

FIG. 2 (color online). Temperature dependence of the in-plane penetration depth $\Delta\lambda_a$ in three single crystals of LaFePO. Data for sample 3 has been multiplied by 1.5. The curves are offset for clarity. Solid lines are power-law fits giving an exponent of 1.2 ± 0.1. The dashed lines are the behavior expected for a fully gapped Fermi surface (a) with parameter relevant to Sm-1111 [5] and (b) the conventional isotropic BCS case. Both curves have been multiplied by 50 for clarity.

temperature behavior is dominated by the smallest gap on the Fermi surface. We show in Fig. 2 the expected temperature dependence from gaps of $1.76T_c$ (the BCS weak-coupling value) and $1.0T_c$, similar to that found in Sm-1111 [5] (in both cases we assume $\lambda_0 \sim 2500$ Å). These show an exponential saturation incompatible with our data. We find that if there is a small residual gap it is at least 30 times smaller than the gap maximum. The presence of nodes is therefore much more likely.

The absolute values of $\Delta\lambda(T)$ are somewhat variable between samples. As shown in Fig. 2, $d\lambda/dT \simeq 350$ Å/Hz in samples 1 and 2 and smaller value of 220 Å/Hz in sample 3. This discrepancy in slope is likely to be due to uncertainties in the calibration factors relating the measured frequency shifts to $\Delta\lambda(T)$ arising from surface roughness. Samples 1 and 2 had significantly rougher surfaces than sample 3 (see Ref. [22]). Alternatively, it could result from intrinsic differences in the superfluid density as a function of doping, i.e., slight changes in the oxygen stoichiometry (T_c of sample 3 was ~0.2 K higher than sample 1). At present no data exist for the evolution of λ_0 with doping.

In the usual weak-coupling theory for superconductors with line nodes, the normalized superfluid density $\tilde{\rho} = [\lambda_0/\lambda(T)]^2$ varies linearly over a much wider range of T than $\lambda(T)$ [corrections to the former are $\mathcal{O}(T^3)$ whereas to the later they are of $\mathcal{O}(T^2)$]. Muon spin relaxation measurements of polycrystalline samples [27] of LaFePO suggest $\lambda_0 \simeq 2400$ Å. Values for the related materials La-1111 [28] and Sm-1111 [29] span the range 2000–3500 Å. In Fig. 3 we plot the temperature dependent part of the superfluid density ($\Delta\tilde{\rho} = 1 - \tilde{\rho}$) multiplied by a scale factor $\lambda_0/2$. For $\lambda_0 = \infty$ this is exactly equal to $\Delta\lambda(T)$ and so the figure shows directly how different assumed values of λ_0 effect the temperature dependence of the superfluid density. The range of λ_0 values plotted encompasses our uncertainty in our calibration factors and also λ_0. A fit of $\tilde{\rho}$ to a power law shows that the exponent is equal to unity within an uncertainty of 5% with λ_0 in the range 2000–4000 Å.

In a nodal superconductor the low temperature behavior is dominated by the excitations near the gap nodes. For a superconductor with line nodes $\lambda(T)$ is linear, with a slope determined by the rate at which the gap grows away from the nodes. In the simple d-wave case with $\Delta_k = \Delta_0 \cos(2\theta)$, $\Delta\lambda = \ln 2 \lambda_0 k_B T/\Delta_0$. For the weak coupling value $\Delta_0 \simeq 2.14 k_B T_c$ this predicts a value of around 100–200 Å/K (for λ_0 in the range quoted above), somewhat smaller than the slope observed experimentally in samples 1 and 2, but close to the value seen in sample 3. As this calculation relies directly on λ_0, better measurements of this parameter are required to make any precise comparisons to this or other candidate gap functions.

Differences in the temperature dependence of λ_c and λ_a can sometimes reveal information about gap symmetry.

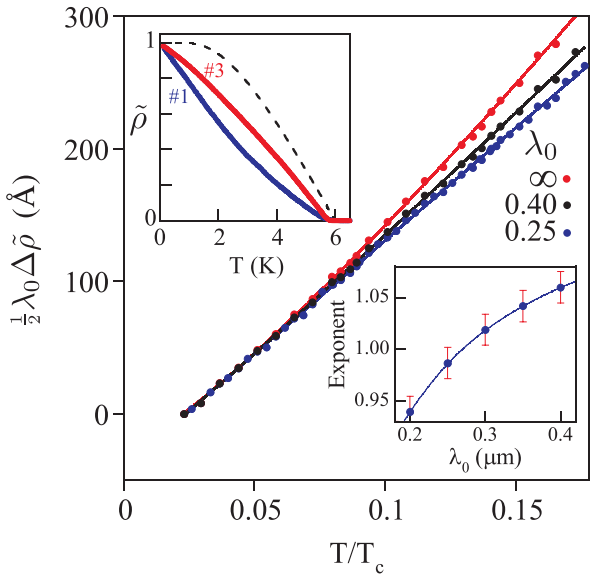

FIG. 3 (color online). Change in normalized superfluid density as a function of assumed value of λ_0 for sample 1. The main panel shows $\frac{1}{2}\lambda_0(\Delta\tilde{\rho})$ for $\lambda_0 = \infty$, 0.25 μm, and 0.4 μm. Upper inset: Normalized superfluid density over the full temperature range for samples 1 and 3 assuming $\lambda_0 = 0.25$ μm. The dashed line shows the behavior found for Sm-1111 [5]. Lower inset: variation of exponent n in power-law fit to superfluid density in range $T = 0.1$–1.0 K.

For example, in multiband systems the c-axis response can also be different due to the presence of sheets with differing anisotropy and different gaps [26,30]. For sample 1 measurements were also performed with the field parallel to the conducting planes. This induces a combination of in-plane and interplane currents and thus probes a mixture of $\Delta\lambda_a$ and $\Delta\lambda_c$. We define $\Delta\lambda_{\rm mix} = \Delta F^{H||a}/(2\alpha\ell_a\ell_b) \simeq \Delta\lambda_a + (\ell_c/\ell_a)\Delta\lambda_c$, where α is a constant relating changes in superconductor volume to the observed frequency shift ($\Delta F^{H||a}$) and ℓ_a, ℓ_b, ℓ_c are the crystal dimensions in the two in-plane and c directions. Sample 1 has $\ell_a/\ell_c \simeq 7$ and so $\Delta\lambda_{\rm mix}$ (shown in Fig. 4) contains a substantial contribution from λ_c. $\Delta\lambda_{\rm mix}$ is 3.6 times larger than $\Delta\lambda_a$ for the same sample but with almost identical temperature dependence. Although the present crystals are not of sufficiently regular geometry to isolate the changes in λ_c precisely, the data are consistent with $\lambda_c(T)$ also having a linear temperature dependence but with a much larger slope due to substantial electronic anisotropy. Measurements of the upper critical field at low temperature indicate an anisotropy $H_{c2}^{||a}/H_{c2}^{||c} \simeq 11$ consistent with the quasi-2D character of the Fermi surface as determined by dHvA measurements [21].

The importance of the observation of a linear T dependence of the superfluid density over a wide range of temperature is that it is very difficult to produce this from extrinsic effects. The identification by Hardy *et al.*

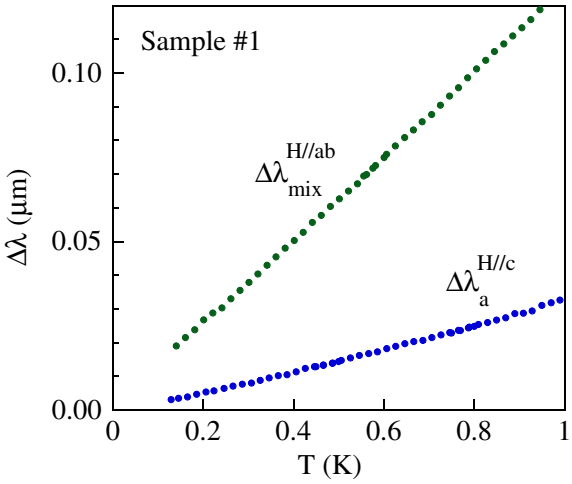

FIG. 4 (color online). Temperature dependence of the penetration depth $\Delta\lambda_{\mathrm{mix}}$ measured with $H||ab$. Data for the same crystal with $H||c$ are also shown for comparison.

[31] of a similar predominately linear behavior of $\lambda(T)$ in $YBa_2Cu_3O_7$ was instrumental in identifying the $d_{x^2-y^2}$ state in the cuprates. Impurities will weaken any intrinsic linear temperature dependence, with $\lambda(T)$ varying like T^2 in the dirty limit [32]. However, power laws with exponent close to 2 can result from, for example, a fully gapped $s_{\pm}$ state with impurities [33]. The impurities produce a nonzero zero energy density of states similar to that found in the d-wave case, and this has been shown to account well for the NMR data [34,35]. Hence, although power laws (with $n \sim 2$) point towards an unconventional gap symmetry they can be produced either with or without nodes. However, the linear dependence observed here strongly points towards nodes.

The observation of an exponential behavior of $\lambda(T)$ is also a robust feature which is not easily mimicked by extrinsic effects, so the different behavior found here for LaFePO compared to the As-based 1111 compounds detailed above, probably points towards these compounds having intrinsically different gap symmetry or anisotropy. Just such a possibility was recently emphasized in the theoretical work of Graser *et al.* [17].

From precise measurements of the penetration depth in clean crystals we have shown strong evidence to suggest that the ferropnictide superconductor LaFePO has nodes in its superconducting gap function. Combined with the detailed information about the full three-dimensional electronic structure of this material derived from dHvA measurements, this should help to decide between competing theories for the origin of superconductivity in these materials.

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Note added.—Recently, we learned of local scanning SQUID susceptibility measurements in LaFePO crystals which also show a linear temperature dependence [36].

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